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(71) Applicant : **CHEMICAL RESEARCH &
LICENSING COMPANY**
10100 Bay Area Boulevard
Pasadena, Texas 77507 (US)

(72) Inventor : **Jones, Edward Maurice, Jr.**
806 Bonnie Doon
Friendswood, Texas 77546 (US)
Inventor : **Smith, Lawrence Alfred, Jr.**
5009 Pine Street
Houston, Texas 77401 (US)
Inventor : **Hearn, Dennis**
16326 Thunderbay
Houston, Texas 77062 (US)
Inventor : **Arganbright, Robert Phillip**
814 Devonport
Seabrook, Texas 77586 (US)

(74) Representative : **Cropp, John Anthony David**
MATHYS & SQUIRE 10 Fleet Street
London, EC4Y 1AY (GB)

(54) **Selective hydrogenation of C5 streams.**

(57) A process for the selective hydrogenation of diolefins contained in a refinery C₅ stream wherein the catalyst used is also a component in a distillation structure. Essentially no hydrogenation of the mono-olefins occurs. Additionally some of the mono-olefins may be isomerized to more valuable isomers of the mono-olefin.

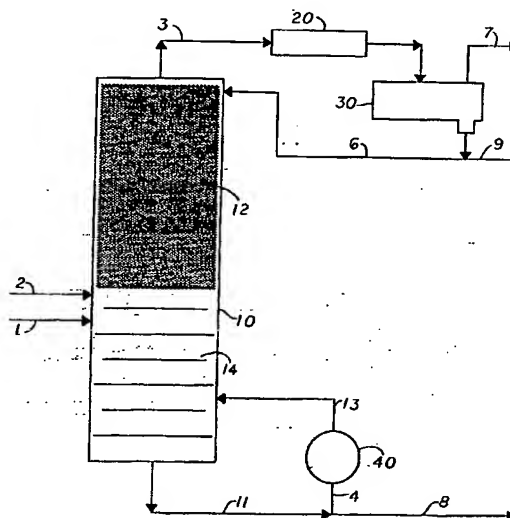


FIG. 1.

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BACKGROUND OF THE INVENTION

Related US Patent No. 5,087,780 discloses the hydroisomerization of mixed C₄ streams and the hydrogenation of butadiene.

Field of the Invention

The present invention relates to the selective hydrogenation of diolefins (dienes) contained in a refinery stream containing predominantly C₆'s and more specifically olefinic C₆'s. More particularly the invention relates to a process for the selective hydrogenation of the dienes utilizing a distillation column reactor containing a hydrogenation catalyst which also acts as a component in a distillation structure. Most specifically the invention relates to the selective hydrogenation of a C₆ feed stream for the production of tertiary amyl methyl ether (TAME). Related Information

Mixed refinery streams often contain a broad spectrum of olefinic compounds. This is especially true of products from either catalytic cracking or thermal cracking processes. These olefinic compounds comprise ethylene, acetylene, propylene, propadiene, methylacetylene, butenes, butadiene, etc. Many of these compounds are valuable, especially as feed stocks for chemical products. Ethylene, especially is recovered. Additionally, propylene and the butenes are valuable. However, the olefins having more than one double bond and the acetylenic compounds (having a triple bond) have lesser uses and are detrimental to many of the chemical process in which the single double bond compounds are used, for example polymerization.

Refinery streams are usually separated by fractional distillation, and because they often contain compounds that are very close in boiling points, such separations are not precise. A C₆ stream, for instance, may contain C₄'s and up to C₈'s. These components may be saturated (alkanes), unsaturated (mono-olefins), or poly-unsaturated (diolefins). Additionally, the components may be any or all of the various isomers of the individual compounds.

Hydrogenation is the reaction of hydrogen with a carbon-carbon multiple bond to "saturate" the compound. This reaction has long been known and is usually done at superatmospheric pressures and moderate temperatures using an excess of hydrogen over a metal catalyst. Among the metals known to catalyze the hydrogenation reaction are platinum, rhenium, cobalt, molybdenum, nickel, tungsten and palladium. Generally, commercial forms of catalyst use supported oxides of these metals. The oxide is reduced to the active form either prior to use with a reducing agent or during use by the hydrogen in the feed. These metals also catalyze other reactions, most notably dehydrogenation at elevated temperatures. Additionally they can promote the reaction of olefinic compounds with themselves or other olefins to produce dimers or oligomers as residence time is increased.

Selective hydrogenation of hydrocarbon compounds has been known for quite some time. Peterson, et al in "The Selective Hydrogenation of Pyrolysis Gasoline" presented to the Petroleum Division of the American Chemical Society in September of 1962, discusses the selective hydrogenation of C₄ and higher diolefins. Boitiaux, et al in "Newest Hydrogenation Catalyst", Hydrocarbon processing, March 1985, presents an overview of various uses of hydrogenation catalysts, including selective hydrogenation, utilizing a proprietary bimetallic hydrogenation catalyst.

Isomerization can be achieved with the same family of catalysts. Generally the relative rates of reaction for various compounds are in the order of from faster to slower:

- (1) hydrogenation of diolefins
- (2) isomerization of the mono-olefins
- (3) hydrogenation of the mono-olefins.

It has been shown generally that in a stream containing diolefins, the diolefins will be hydrogenated before isomerization occurs.

The use of a solid particulate catalyst as part of a distillation structure in a combination distillation column reactor for various reactions is described in U.S. Pat. No.s: (etherification) 4,232,177; 4,307,254; 4,336,407; 4,504,687; 4,918,243; and 4,978,807; (dimerization) 4,242,530; (hydration) 4,982,022; (dissociation) 4,447,668; and (aromatic alkylation) 4,950,834 and 5,019,669. Additionally U.S. Pat. No.s 4,302,356 and 4,443,559 disclose catalyst structures which are useful as distillation structures.

The C₆ refinery cut is valuable as a gasoline blending stock or as source of isoamylene to form an ether by reaction with lower alcohols. Tertiary amyl methyl ether (TAME) is rapidly becoming valuable to refiners as a result of the recently passed Clean Air Act which sets some new limits on gasoline composition. Some of these requirements are (1) to include a certain amount of "oxygenates", such as methyl tertiary butyl ether (MTBE), TAME or ethanol, (2) to reduce the amount of olefins in gasoline, and (3) to reduce the vapor pressure (volatility).

The C₅'s in the feed to a TAME unit are contained in a single "light naphtha" cut which contains everything from C₅'s through C₈'s and higher. This mixture can easily contain 150 to 200 components and thus identification and separation of the products is difficult. Usually the C₅'s and a small part of the C₆'s are separated for use in the TAME process. However, the incorporation of C₆ through C₈ tertiary olefins will allow the production of other valuable ether products. For this reason the TAME is not separated from the heavier components, but all are used directly as octane blending stocks.

Several of the minor components (diolefins) in the feed will react slowly with oxygen during storage to produce "gum" and other undesirable materials. However, these components also react very rapidly in the TAME process to form a yellow, foul smelling gummy material. Thus it is seen to be desirable to remove these components whether the "light naphtha" cut is to be used only for gasoline blending by itself or as feed to a TAME process.

It is an advantage of the present hydrogenation process which selectively hydrogenates diolefins that little if any saturation of the mono-olefins occurs. An additional feature of the process is that a portion of the mono-olefins contained within the stream or produced by the selective hydrogenation of the diolefins are isomerized to more desirable products.

SUMMARY OF THE INVENTION

Briefly, the present invention comprises feeding a light naphtha cut containing a mixture of hydrocarbons along with a hydrogen stream to a distillation column reactor containing a hydrogenation catalyst which is a component of a distillation structure and selectively hydrogenating the diolefins contained in the light naphtha. Concurrently the lighter components, including the unreacted hydrogen, are distilled and separated as overheads from the partially hydrogenated light naphtha product. Additionally and concurrently with the selective hydrogenation and distillation, a portion of the C₅ mono-olefins are isomerized to a more desirable feed for the TAME. Essentially all of the diolefins are converted to mono-olefins with very little hydrogenation of the mono-olefins.

In one embodiment where the feed is predominately a C₅ stream the light naphtha product is withdrawn as bottoms. The overheads are passed to a condenser in which all of the condensibles are condensed and a portion refluxed to the top of the column.

In a second embodiment where the feed comprises a broader C₅ to C₈ stream the C₅'s are separated from the C₆+ components in the lower section of a distillation column reactor. The C₆+ components are withdrawn as a bottoms stream while the C₅'s are boiled up into the upper section of the distillation column reactor which contains the catalytic distillation structure which selectively hydrogenates the diolefins. The hydrogenated C₅'s are taken overheads along with the excess hydrogen and passed to the condenser in which all of the condensibles are condensed and subsequently separated from the uncondensibles (mostly hydrogen), for example in a reflux drum separator. A portion of the liquid from the separator is returned to the distillation column reactor as reflux and the remainder withdrawn as product which may be directly charged to a TAME unit. If desired a further inert distillation section may be utilized above the catalytic distillation structure with a C₅ product side draw below to fractionate out the excess hydrogen along with any other light components such as air, water, etc. which might be troublesome in the downstream TAME unit.

Broadly the present invention is a process for the selective hydrogenation of diolefins contained in a light naphtha comprising the steps of:

(a) feeding (1) a first stream comprising a light naphtha containing diolefins and (2) a second stream containing hydrogen to a distillation column reactor into a feed zone;

(b) concurrently in said distillation column reactor

(i) contacting said first and second streams in a distillation reaction zone with a hydrogenation catalyst capable of acting as a distillation structure, thereby reacting essentially all of said diolefins with said hydrogen to form pentenes and other hydrogenated products in a reaction mixture, and

(ii) operating the pressure of the distillation column reactor such that a portion of the mixture is vaporized by the exothermic heat of reaction;

(c) withdrawing a portion of the liquid from step (b) (ii) from said distillation column reactor as bottoms; and

(d) withdrawing the vapors from step (b) (ii) along with any unreacted hydrogen from said distillation column reactor as overheads.

Hydrogen is provided as necessary to support the reaction and to reduce the oxide and maintain it in the hydride state. The distillation column reactor is operated at a pressure such that the reaction mixture is boiling in the bed of catalyst. A "froth level" may be maintained throughout the catalyst bed by control of the bottoms and/or overheads withdrawal rate which improves the effectiveness of the catalyst thereby decreasing the

height of catalyst needed. As may be appreciated the liquid is boiling and the physical state is actually a froth having a higher density than would be normal in a packed distillation column but less than the liquid without the boiling vapors.

The present process preferably operates at overhead pressure of said distillation column reactor in the range between 0 and 250 psig and temperatures within said distillation reaction zone in the range of 100 to 300°F, preferably 130 to 270°F.

The C₅ feed and the hydrogen are preferably fed to the distillation column reactor separately or they may be mixed prior to feeding. A mixed feed is fed below the catalyst bed or at the lower end of the bed. Hydrogen alone is fed below the catalyst bed and the C₆ stream is fed below the bed to about the mid one-third of the bed. The pressure selected is that which maintains the dienes in the catalyst bed while allowing the propylene and lighter to distill overhead.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a simplified flow diagram of one embodiment of the present invention.

FIG. 2 is a simplified flow diagram of a second embodiment of the present invention.

FIG. 3 is a simplified flow diagram of a third embodiment of the present invention.

FIG. 4 is a simplified flow diagram of a fourth embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The advantages of utilizing a distillation column reactor in the instant selective hydrogenation process lie in the better selectivity of diolefin to olefin, conservation of heat and the separation by distillation which can remove some undesirable compound, e.g. heavy sulfur contaminants, from the feed prior to exposure to the catalyst and the distillation can concentrate desired components in the catalyst zone. The diolefins contained in the C₆ cut are higher boiling than the other compounds and therefore can be concentrated in the catalyst zone while the mono-olefins are isomerized and removed in the upper part of the column. The reactions of the C₅'s of interest are:

- (1) isoprene (2-methyl butadiene-1,3) + hydrogen to 2-methyl butene-1 and 2-methyl butene-2;
- (2) cis- and trans 1,3-pentadienes (cis and trans piperylenes) + hydrogen to pentene-1 and pentene-2;
- (3) 3-methyl butene-1 to 2-methyl butene-2 and 2-methyl butene-1;
- (4) 2-methyl butene-1 to 2-methyl butene-2;
- (5) 2-methyl butene-2 to 2-methyl butene-1; and
- (5) 1,3-butadiene to butene-1 and butene-2.

The first two reactions remove the undesirable components while the third is advantageous for feed to a TAME reactor. The 3-methyl butene-1 does not react with methanol to produce TAME over the sulfonic acid catalyst while the two 2-methyl butenes do.

The catalytic material employed in the hydrogenation process must be in the form to serve as distillation packing. Broadly stated, the catalytic material is a component of a distillation system functioning as both a catalyst and distillation packing, i.e., a packing for a distillation column having both a distillation function and a catalytic function.

The reaction system can be described as heterogenous since the catalyst remains a distinct entity. The catalyst may be employed as palladium oxide, preferably 0.1 to 1.0 weight %, supported on an appropriate support medium such as alumina, carbon or silica, preferably in containers as described herein or as conventional distillation packing shapes as Raschig rings, Pall rings, saddles or the like.

It has been found that placing the supported catalyst into a plurality of pockets in a cloth belt, which is supported in the distillation column reactor by open mesh knitted stainless steel wire by twisting the two together into a helix, allows the requisite flows, prevents loss of catalyst, allows for normal swelling if any, of the catalyst and prevents breakage of the extrudates through mechanical attrition. This novel catalyst arrangement is described in detail in commonly owned US Patent No. 4,242,530 and US Pat. No. 4,443,559 which are incorporated herein.

The cloth may be of any material which is not attacked by the hydrocarbon feeds or products or catalyst under the conditions of the reaction. Cotton or linen may be useful, but fiber glass cloth or TEFLON cloth is preferred. A preferred catalyst system comprises a plurality of closed cloth pockets arranged and supported in the distillation column reactor by wire mesh intimately associated therewith.

Another suitable container consists of metal or plastic screen of suitable mesh size formed in a short cylinder, closed at each end, in which the catalyst is retained. A plurality of these catalyst containing containers may be packed randomly or in a regular fashion into a bed within the distillation column reactor. There may be

one or more of such beds, depending on the catalyst requirements of the process.

The particulate catalyst material may be a powder, small irregular chunks or fragments, small beads and the like. The particular form of the catalytic material in the containers is not critical, so long as sufficient surface area is provided to allow a reasonable reaction rate. The sizing of catalyst particles should be such that the catalyst is retained within the containers.

A catalyst suitable for the present process is 0.34 wt% Pd on 3 to 8 mesh Al_2O_3 (alumina) spheres, supplied by United Catalysts Inc. designated as G-68C. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE I

Designation	G-68C
Form	Sphere
Nominal size	5x8 mesh
Pd. wt%	0.3 (0.27-0.33)
Support	High purity alumina

The catalyst is believed to be the hydride of palladium which is produced during operation. The hydrogen rate to the reactor must be sufficient to maintain the catalyst in the active form because hydrogen is lost from the catalyst by hydrogenation. The hydrogen rate must be adjusted such that it is sufficient to support the hydrogenation reaction and replace hydrogen lost from the catalyst but kept below that which would cause flooding of the column which is understood to be the "effectuating amount of hydrogen" as that term is used herein. Generally the mole ratio of hydrogen to diolefins in the feed to the fixed bed of the present invention will be at least 1.0 to 1.0 preferably 2.0 to 1.0.

The present invention carries out the method in a catalyst packed column which can be appreciated to contain a vapor phase ascending and some liquid phase as in any distillation. However since the liquid is held up within the column by artificial "flooding", it will be appreciated that there is an increased density over that when the liquid is simply descending because of what would be normal internal reflux.

Referring now to FIG. 1 there is shown a simplified flow diagram in schematic of a preferred embodiment. There is shown a distillation column reactor 10 containing a packing of suitable hydrogenation catalyst as part of a distillation structure 12, as in the wire mesh arrangement described above. The column may also have standard distillation structure 14. The light naphtha is fed via line 1 to the distillation column reactor 10 below the catalyst packing. The hydrogen is fed as a gas via flow line 2 at or near the bottom of the bed of catalyst packing. Heat is added to the bottoms via flow line 4 by circulating through the reboiler 40 and back to the column via flow line 13. After the reaction has started the heat of reaction, which is exothermic, causes additional vaporization of the mixture in the bed. Vapors are taken overhead through flow line 3 and passed to condenser 20 where substantially all of the condensable material is condensed to a temperature of 100°F. The overheads are then passed to reflux drum 30 where the condensed material is collected and separated from non condensibles, such as the unreacted hydrogen. A portion of the condensed materials collected in the reflux drum are returned to the top of the distillation column reactor 10 via flow line 6. The distillate product, withdrawn through line 9, is a suitable feed for a TAME reactor. The uncondensable material is vented from the reflux drum via flow line 7 and for economy the hydrogen can be recycled to the reactor (not shown).

Bottoms product containing essentially no C_5 diolefins is withdrawn via flow line 8 and may be sent to gasoline blending as stable gasoline. The process is advantageous because the high heat of hydrogenation is absorbed by the vaporization of part of the liquid, so temperature control is achieved by adjusting the system pressure. All excess hydrogen is stripped from the bottoms product. In the case of C_6 's, the unhydrogenated components are less volatile and tend to stay in the reactor for a longer time assisting in more complete reaction.

In FIG. 2, there is shown a second embodiment of the invention wherein the light naphtha is fed to the column 10 above the catalytic distillation structure 12 via flow line 1'. Otherwise the arrangement is identical to FIG. 1. FIG. 3 illustrates a third embodiment wherein the column includes additional conventional distillation structure 216 above the catalytic distillation structure 12 to separate any C_4 and lighter material, hydrogen, and other lower boiling components from the C_5 's which are withdrawn as side stream via flow line 209.

EXAMPLE 1

A three inch diameter 30 foot tall steel column 310 with a reboiler 340, condenser 320 and reflux system 330 and 306 is used as shown in FIG. 4. The middle 15 feet are packed with a catalytic distillation structure 312 comprising 0.34 wt% palladium on 1/8 inch alumina spherical catalyst which is contained in the pockets of a fiber glass belt and twisted with stainless steel wire mesh. The column is purged with nitrogen and pressure up to 20 psig. Light naphtha feed which has been prefractionated to remove most of the C_6+ material is started to the column via line 301 at 50 lbs/hr. When a bottom level is obtained and the liquid is at the desired level in the column, bottoms draw through line 308 is started and reboiler circulation began through line 304 and 313. Heat is added to the reboiler 340 until vapor is seen at the top of the column as evidenced by a uniform temperature of 130°F throughout the column. Hydrogen flow is started to the bottom of the column at between 8 to 10 SCFH via line 302. The pressure on the column is then controlled to maintain a bottoms temperature of about 320°F and a catalyst bed temperature of about 260°F. The overhead pressure was thus maintained about 200 psig. The overheads are taken via line 303 and partially condensed in condenser 320 and all of the condensibles collected in reflux drum 330 and returned to the top of the column as reflux via line 306. Uncondensibles are vented from the drum via line 307. Liquid bottoms are withdrawn via line 308. The results are shown in TABLE II below in which the feed and bottoms analyses are compared.

TABLE II

Component, wt%	Feed	Bottoms Product	% Change
Lights	0.073	0.000	-100
Dimethyl ether	0.003	0.002	-36
isobutane	0.488	0.093	-81
methanol	0.058	0.000	-100
Other C_4 's	4.573	3.304	-28
3-methyl butene-1	1.026	0.270	-74
isopentane	31.974	32.066	0
pentene-1	2.708	0.962	-64
2-methyl butene-1	6.496	4.012	-38
normal pentane	3.848	4.061	6
2-methyl butadiene-1,3	0.147	0.002	-99
trans pentene-2	6.995	9.066	30
Unknown 1	0.138	0.094	-32
cis pentene-2	3.886	3.723	-4
2-methyl butene-2	11.634	14.083	21
trans piperylene	0.142	0.002	-98
cis piperylene	0.095	0.003	-97
cyclo- C_6	0.001	0.058	-47
C_6+	25.603	28.198	10
Total	100.000	100.000	

Example 2

During the run the overhead pressure was adjusted to vary the catalyst bed temperature. At lower temperatures the conversion of the diolefins was lower, but the main difference was that the isomerization of the 3-methyl butene-1 was more dramatically affected. Table III below compares the conversions of the diolefins and 3-methyl butene-1 with the operating temperature.

TABLE III						
Mid. Temp °F	OH Press psig	Hrs on STM	Conversion, Mole %			
			isoprene	t-Pip	c-Pip	3-methyl butene-1
230	130	200	65	57	65	17
250	145	300	97	95	95	55
265	200	600	100	99	99	80

Claims

1. A process for the selective hydrogenation of diolefins contained in a light naphtha comprising the steps of:
 - (a) feeding (1) a first stream comprising a light naphtha containing diolefins and (2) a second stream containing hydrogen to a distillation column reactor into a feed zone;
 - (b) concurrently in said distillation column reactor
 - (i) contacting said first and second streams in a distillation reaction zone with a hydrogenation catalyst capable of acting as a distillation structure thereby reacting essentially all of said diolefins with said hydrogen to form pentenes and other hydrogenated products in a reaction mixture, and
 - (ii) operating the pressure of the distillation column reactor such that the temperature in said distillation reaction zone is in a selected range and a portion of the mixture is vaporized by the exothermic heat of reaction;
 - (c) withdrawing the liquid portion from step (b) (ii) from said distillation column reactor as bottoms; and
 - (d) withdrawing the vaporous portion from step (b) (ii) along with any unreacted hydrogen from said distillation column reactor as overheads.
2. The process according to claim 1 wherein said overheads are cooled to condense any condensible material and said condensible material is separated from said unreacted hydrogen and returned to the upper portion of said distillation column as reflux.
3. The process according to claim 2 wherein the vaporous portion from step (b) contains substantially all of the C₆ and lighter boiling fraction and the liquid from step (b) contains substantially all of the C₆ and heavier boiling fraction and said condensible material comprises C₅'s.
4. The process according to claim 3 wherein a portion of said condensible material is withdrawn as, distillate product.
5. The process according to any one of claims 2 to 4 wherein said separated hydrogen is recycled to said distillation column reactor.
6. The process according to any one of claims 1 to 5 wherein said hydrogenation catalyst comprises 0.34 wt% palladium oxide supported on 1/8 inch alumina spheres and said hydrogenation catalyst is contained in the pockets of a cloth belt which is twisted with distillation wire to form a catalytic distillation structure and placed into said distillation column reactor.
7. The process according to any one of claims 1 to 6 wherein hydrogen is contained in said second stream in an amount to provide a mole ratio of hydrogen to said diolefins of from 1:1 to 2:1.

8. The process according to any one of claims 1 to 7 wherein the overhead pressure of said distillation column reactor is between 0 and 250 psig.
9. The process according to claim 8 wherein the temperature within said distillation reaction zone is between 100 and 300°F.
10. The process according to any one of claims 1 to 9 wherein said pentenes comprise 3-methyl butene-1 and 2-methyl butene-2, and a portion of said 3-methyl butene-1 is isomerized to 2-methyl butene-2.
11. The process according to any one of claims 1 to 10 wherein a distillate product containing C₆'s is withdrawn as a side stream below the top of said distillation column reactor.
12. A process for selective hydrogenation of diolefins and isomerization of mono-olefins contained within a light naphtha, comprising the steps of:
 - (a) feeding (1) a first stream comprising a light naphtha and containing 3-methyl butene-1, 2-methyl butene-1, 2-methyl butene-2, 2-methyl butadiene-1,3, cis 1,3-pentadiene and trans 1,3-pentadiene and (2) a second stream containing hydrogen to a distillation column reactor into a feed zone;
 - (b) concurrently in said distillation column reactor
 - (i) contacting said first and second streams in a distillation reaction zone with a hydrogenation catalyst acting as a distillation structure thereby reacting essentially all of said 2-methyl butadiene, cis 1,3-pentadiene and trans 1,3-pentadiene with said hydrogen to form pentenes and isomerizing a portion of said 3-methyl butene-1 to form 2-methyl butene-2 in a reaction mixture, and
 - (ii) controlling the overhead pressure of the distillation column reactor at a pressure of about 200 psig such that the temperature of the mixture within said distillation reaction zone is between 250-270°F and a portion of the mixture is vaporized by the exothermic heat of reaction;
 - (c) withdrawing the liquid portion from step (b) (ii) from said distillation column reactor as bottoms; and
 - (d) withdrawing the vaporous portion from step (b) (ii) along with any unreacted hydrogen from said distillation column reactor as overheads.
13. The process according to claim 12 wherein said overheads are cooled to condense any condensible material and said condensible material is separated from said unreacted hydrogen and returned to the upper portion of said distillation column as reflux.
14. The process according to claim 13 wherein said separated hydrogen is recycled to said distillation column reactor.
15. A process for the selective hydrogenation of diolefins contained in a light naphtha comprising the steps of:
 - (a) feeding (1) a first stream comprising a light naphtha containing diolefins and (2) a second stream containing hydrogen to a distillation column-reactor into a feed zone;
 - (b) concurrently in said distillation column reactor
 - (i) contacting said first and second streams in a distillation reaction zone with a hydrogenation catalyst comprising palladium oxide supported on alumina particles and said hydrogenation catalyst is contained in the pockets of a cloth belt which is twisted with distillation wire to form a catalytic distillation structure, thereby reacting essentially all of said diolefins with said hydrogen to form pentenes and other hydrogenated products in a reaction mixture, and
 - (ii) controlling the overhead pressure of the distillation column reactor in the range of 130 to 210 psig such that the temperature in said distillation reaction zone is between 230 and 270°F and a portion of the mixture is vaporized by the exothermic heat of reaction;
 - (c) withdrawing a first portion of the liquid from step (b) (ii) from said distillation column reactor as bottoms;
 - (d) withdrawing a second portion of the liquid from step (b) as a side stream;
 - (e) withdrawing the vaporous portion from step (b) (ii) along with any unreacted hydrogen from said distillation column reactor as overheads;
 - (f) cooling said overheads to condense all of the compounds that condense at that temperature and said overhead pressures of between 130 and 210 psig;
 - (g) separating said condensed material from any uncondensed material in said overheads and returning a portion of said condensed material to said distillation column reactor as reflux;

(h) withdrawing the remaining portion of said condensed material as a distillate product; and
(i) recycling any unreacted hydrogen contained in said uncondensed material to said distillation column reactor.

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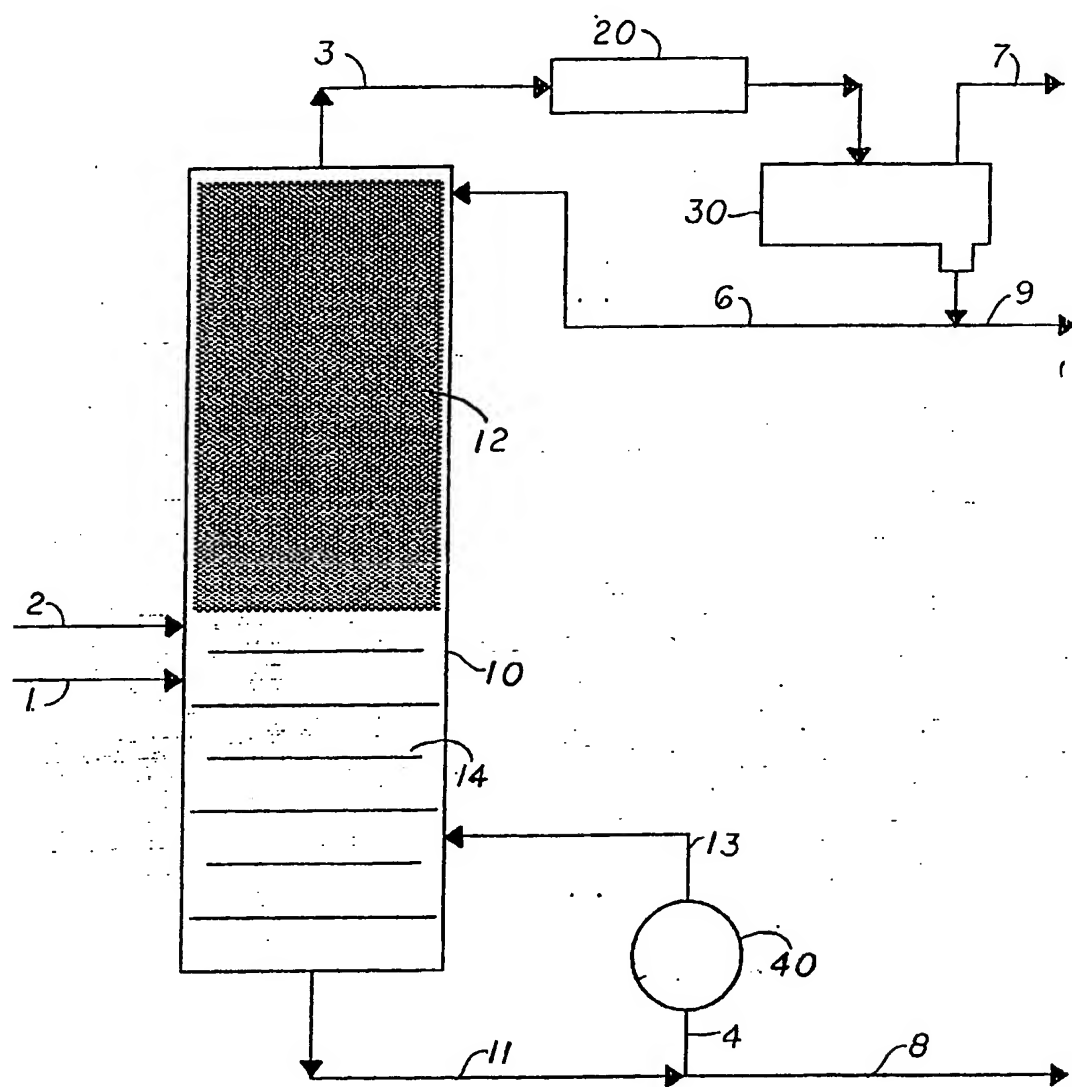


FIG. 1.

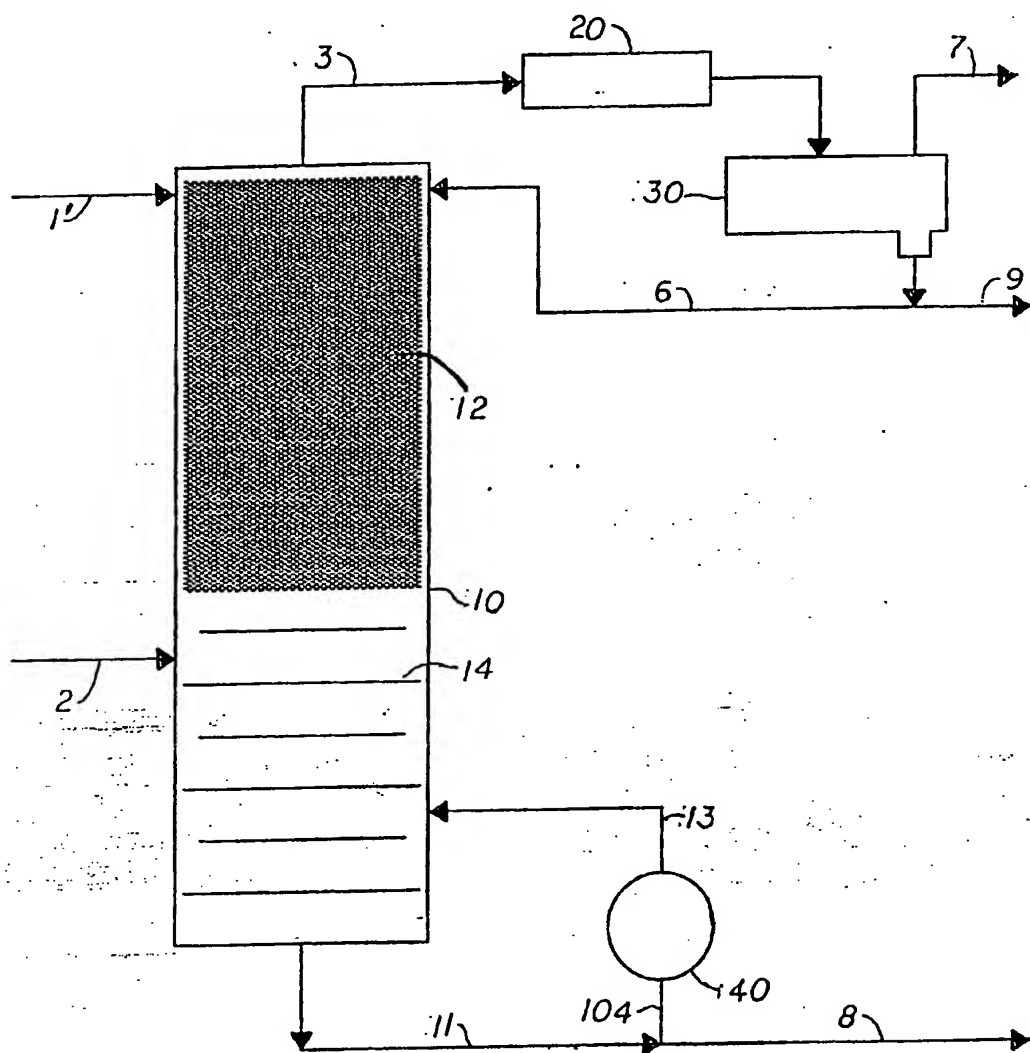


FIG. 2

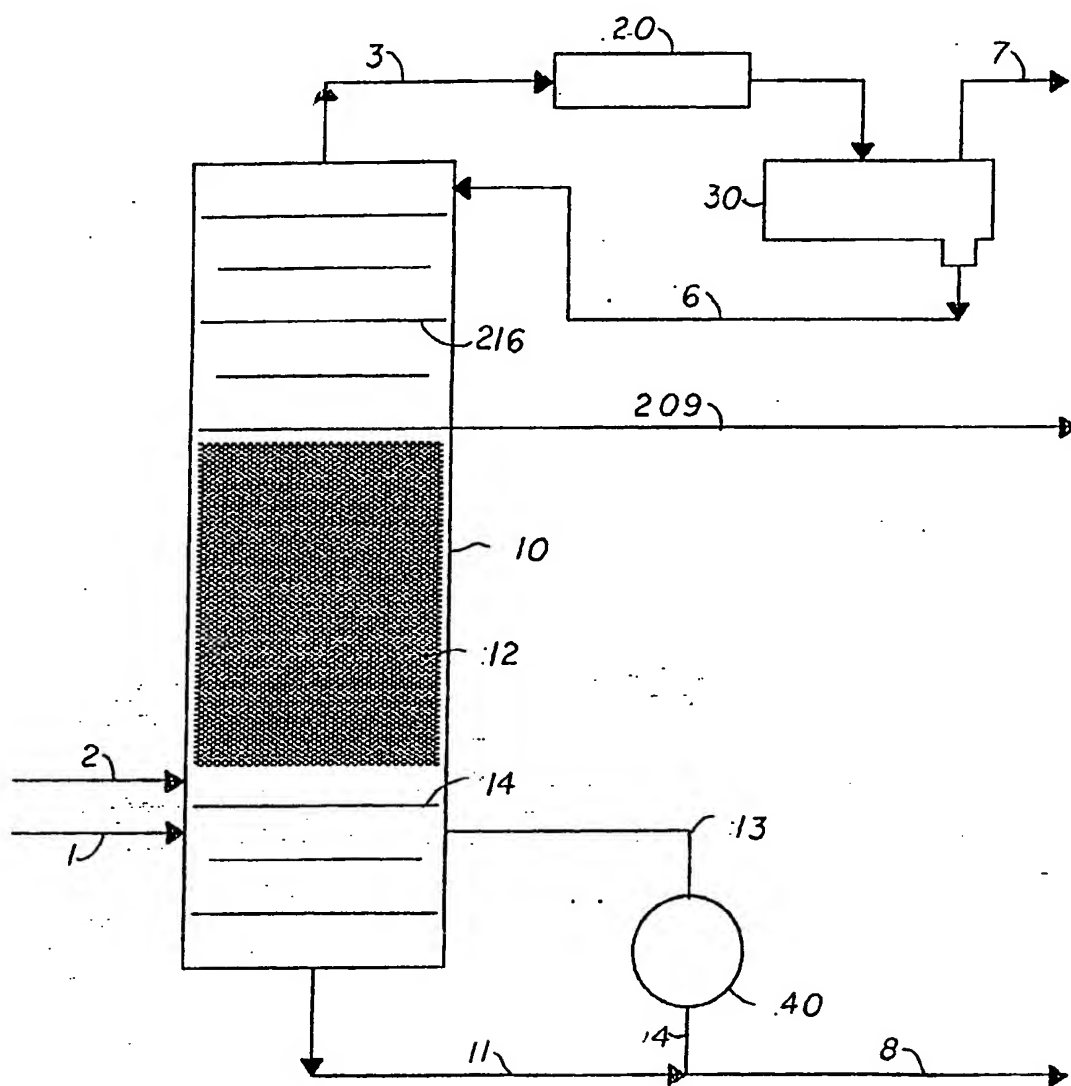


FIG. 3

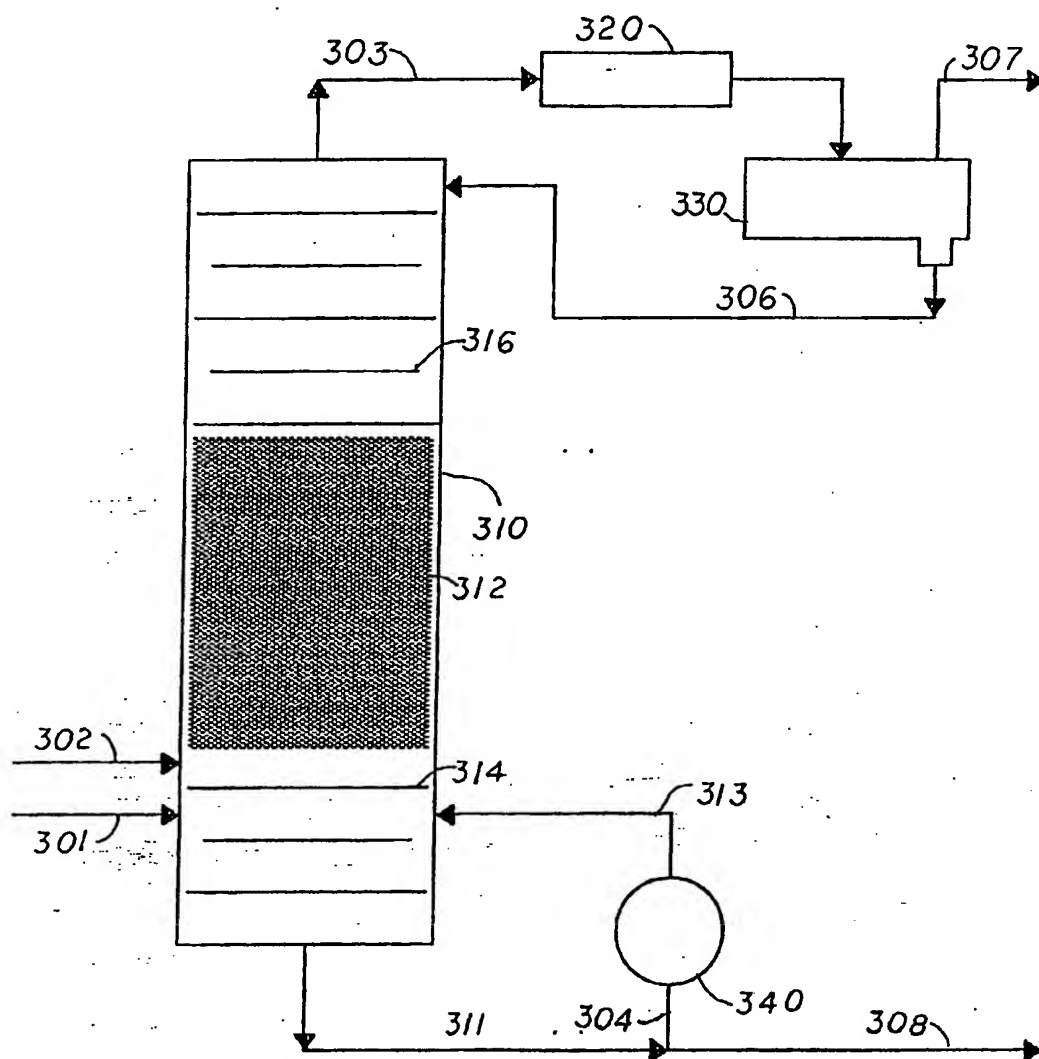


FIG. 4



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 0939

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. CLS)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, P, X	US-A-5 087 780 (CHEMICAL RESEARCH) * the whole document *	1-15	C10G45/32
Y	US-A-4 443 559 (CHEMICAL RESEARCH & LICENSING) * the whole document *	1-15	
Y	FR-A-1 302 069 (HOECHST) * the whole document *	1-15	
A	EP-A-0 008 860 (CHEMICAL RESEARCH AND LICENSING) * claims 1-6; figures 1-3.* -----	1-15	
			TECHNICAL FIELDS SEARCHED (Int. CLS)
			C10G C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 12 MAY 1993	Examiner MICHIELS P.	
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